

Singerman, Joel

From: Brown, Janet E (DEC) <janet.brown@dec.ny.gov>
Sent: Friday, October 22, 2021 9:40 AM
To: Singerman, Joel
Cc: Garbarini, Doug
Subject: FW: Draft talking points for 10/26/21 CAG meeting
Attachments: Talking Points_for 10-26-2021 - CAG meeting.docx;
VOCs_From_Coal_Tar_and_Soil_Vapor_Samples-at_MGP_Sites.pdf; Figure 1. DRAFT Site Remediation Plan_rev 2021-10-21.pdf

Hi Joel, When I sent the below/attd to Doug this am, I rec'd his out of office reply, so forwarding along to you in the interest of time.

Regards,
Janet

From: Brown, Janet E (DEC)
Sent: Friday, October 22, 2021 8:52 AM
To: Garbarini, Doug <Garbarini.Doug@epa.gov>
Cc: Eaton, Daniel J (DEC) <daniel.eaton@dec.ny.gov>; Deyette, Scott (DEC) <scott.deyette@dec.ny.gov>; Miller, John Y (DEC) <john.miller@dec.ny.gov>
Subject: Draft talking points for 10/26/21 CAG meeting

Doug – Attached are draft talking points to be delivered by EPA as an update on our discussions at the 10/26 CAG meeting. I understand from our call yesterday that EPA will review these and will be developing a final list of talking points that you will provide to DEC for review/input prior to the CAG meeting. Also attached, as referenced in the talking points, are the SV at MGP sites article that you provided to us the other day and the figure that Grid developed summarizing remedial work. Please let us know if you have any questions.

Thx,
Janet

Contributed Articles

Volatile Organic Compounds from Coal Tar and Soil Vapor Samples at MGP Sites

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This study characterized organic compounds found in New York State manufactured gas plant (MGP) coal tar vapors using controlled laboratory experiments from four separate MGP sites. In addition, a limited number of deep (0.3–1.2 m above coal tar) and shallow (1.2–2.4 m above coal tar) soil vapor samples were collected above the *in situ* coal tar source at three of these sites. A total of 29 compounds were consistently detected in the laboratory-generated coal tar vapors at 50°C, whereas 24 compounds were detected at 10°C. The compounds detected in the field sample results were inconsistent with the compounds found in the laboratory-generated samples. Concentrations of compounds in the shallow soil vapor sample were either non-detectable or substantially lower than those found in deeper samples, suggesting attenuation in the vadose zone. Laboratory-generated data at 50°C compared the (% non-aromatic)/(% aromatic) ratio and indicated that this ratio may provide good discrimination between coal tar vapor and common petroleum distillates.

Keywords: coal tar, soil vapor, attenuation, benzene, naphthalene

Introduction

There are approximately 300 manufactured gas plant (MGP) sites in New York State. MGPs were industrial facilities that produced gas from coal, oil, and other feedstocks. MGPs began operating in the United States in the early 1800s. Coal gas from MGPs was initially used for lighting, transitioning to a source of fuel for heating and cooking following the introduction of electricity in the late 1800s. It was eventually replaced by natural gas for these and other uses in the early to mid-1900s. Coal gas was stored at the MGP in vessels known as gas holders from which they were distributed through a network of pipes to the local population (Hayes et al., 1996; New York State Department of Environmental Conservation [NYS DEC], 2013).

Production of manufactured gas created a number of different byproducts and wastes, such as coal tar, which was a dense hydrocarbon liquid. The coal tar was separated from the gas

following production, with additional separation taking place during storage and distribution. This coal tar was collected at various points in the process and was often recycled as a fuel within the MGP and sometimes sold for use as a lumber preservative or roofing material. Coal tar produced in excess of these internal and external demands was managed on site in pits or other land-based facilities, from which it could contribute to the contamination of soil, groundwater, surface water, and sediments (Hayes et al., 1996).

Coal tar contains a number of different classes of chemical constituents that are a potential cause for concern when left untreated in the environment. The two primary classes of constituents typically investigated at an MGP site are: 1) volatile organic compounds (VOCs) such as benzene, toluene, ethylbenzene, and xylenes (BTEX compounds); and 2) semi-volatile organic compounds (SVOCs) such as polycyclic aromatic hydrocarbons (PAHs), specifically naphthalene (Hayes et al., 1996; United States Environmental Protection Agency [EPA] 1999a; NYS DEC 2013).

Soil vapor intrusion (SVI) is a term that refers to the migration of VOCs and SVOCs in soil vapor from the subsurface into overlying buildings, where individuals may come into contact with the VOCs and SVOCs in the indoor air (ITRC 2007). New York State finalized its guidance for evaluating

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Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/uenf.

SVI at sites, including MGP sites, in 2006 (NYS DOH 2006). The analytical method most often used in the sample analysis during these investigations is EPA Method TO-15, which measures approximately 60 different VOC compounds (EPA 1999b). For MGP site investigations, EPA Method TO-15 is often modified to include compounds such as indane, indene, and naphthalene. Naphthalene is commonly classified as SVOCs, as its vapor pressure (0.083 Torr) is slightly below the recommended 0.1 Torr lower limit listed in the method (EPA 1999b). However, despite its lower vapor pressure, studies have shown that EPA Method TO-15 can be successfully applied to microgram per cubic m ($\mu\text{g}/\text{m}^3$) concentrations of naphthalene in air (Hayes and Benton 2007). The typical remedial investigation strategy to evaluate SVI begins with the collection of exterior soil vapor samples (outside of the building) and the laboratory analysis of the soil vapor using the modified EPA Method TO-15. Based on these soil vapor sampling results, in conjunction with other environmental data and relevant site information, the NYS DEC and/or NYS DOH may recommend SVI sampling of outdoor air, indoor air and sub-slab vapor.

The goals of the study were to: 1) characterize chemical constituents of coal tar vapors in a controlled laboratory experiment; 2) assess the comparability between analytes and concentrations detected in field soil vapor samples collected directly above coal tar sources to those in the controlled laboratory experiment of coal tar vapors; 3) assess the distribution of chemical groups in the coal tar vapors to evaluate whether they can be reliably differentiated from common petroleum distillates; and 4) evaluate whether specific "marker compounds" measured in the coal tar vapors could be used to identify likely MGP-related contaminants in soil vapor samples. The results from the laboratory characterization of coal tar vapor measurements reported in this study are being used to inform the analyte list for MGP-related compounds in a subsequent publication summarizing the results of soil vapor and SVI investigations that were conducted at 83 different MGP site across New York State.

Methods

Sample Collection

The study design included the collection of samples from four different MGP sites in New York State. Each of the sites had two or more locations where coal tar was known to be present in the vadose zone, with a sufficient vadose zone to collect soil vapor samples at intervals of approximately 0.3 and 1.5 m above the tar zone. The four MGP sites (confidential clients) were distributed across New York State. At each of the four sites, the following samples were designated for collection: 1) Two coal tar samples from the vadose zone; 2) Two vadose zone soil vapor samples approximately 0.3 m above the coal tar ("deep" soil vapor sample); and 3) Two vadose zone soil vapor samples approximately 1.5 m above the coal tar

("shallow" soil vapor sample). Due to site-specific variation and other heterogeneities in the subsurface, these vertical distances were approximate.

The depth to the coal tar was estimated at each site using historical boring logs. These estimates were verified in the field prior to sampling using direct push techniques (e.g., Geoprobe, Salina, KS, USA). Coal tar samples were collected and preserved for laboratory analysis in two 250-mL wide-mouth glass jars, which were filled to the top with minimal headspace. All tar samples were stored cold (2°C to 4°C) during transport to the analytical laboratory.

Field measurements were taken to verify the soil vapor sampling locations, which were targeted to be at depths of approximately 0.3 and 1.5 m above the MGP tar sample. The results of these field measurements were used to guide and confirm the final depth for the collection of the soil vapor samples for the study. All soil vapor samples were collected above the *in situ* source, with minimal horizontal offset, at depths ranging from 0.3 to 4.1 m below ground surface. Certified 6-L Summa (Cinnaminson, NJ) canisters with flow controllers and fittings for 1/4-inch outer diameter tubing were provided by the NYS DOH Wadsworth Center Laboratory (Albany, NY). Flow controllers were set for a two-hour sampling duration for each soil vapor sample. Helium tracer field measurements were used to verify the surface seal, in accordance with NYS DOH Guidance (NYS DOH 2006).

Laboratory Analyses

The NYS DOH Wadsworth Center Laboratory conducted all laboratory analyses. The sample preparation and analysis protocols were designed to be comparable to those used during an earlier study, which was also conducted by the NYS DOH Wadsworth Center Laboratory (NYS DOH 2003a). The analyses included: 1) EPA Method TO-15 analysis of coal tar vapors from eight laboratory samples equilibrated to 10°C and eight equilibrated to 50°C; and (2) EPA Method TO-15 analysis of 12 field soil vapor samples (Two deep soil vapor samples and two shallow soil vapor samples at each of three sites. No soil vapor samples were collected at one of the MGP sites due to high water table at the time of sample collection.)

The laboratory-generated coal tar off-gases were conducted using the following procedure. Coal tar-impacted soil was transferred to pre-cleaned 2.5-L wide mouth screw cap Toxicity characteristic leaching procedure (TCLP) extraction vessels that were purged with laboratory-grade zero nitrogen prior to sample loading. After loading, the samples were placed into 10°C and 50°C incubators for 24 hours to encourage volatilization of the tar vapors into the headspace. Immediately following incubation, 0.5 Ls of headspace air was drawn from each extraction vessel into separate evacuated 6-L Summa™ whole air canisters and diluted to 12 Ls by pressurizing to 15 lbs per square inch gauge pressure (psig) using laboratory-grade zero nitrogen. The reported concentration results were corrected for this dilution. The canister samples were allowed

to sit for 24 hours at room temperature to equilibrate and were then analyzed following standard EPA Method TO-15 protocol.

The EPA Method TO-15 protocol included the following process: Summa whole air canisters were connected to the inlet fitting of the Tekmar AutoCan concentrator (Mason, OH) / Agilent (Santa Clara, CA) 6890/5973 gas chromatography/mass spectrometry (GC/MS) analytical system. Compounds in the coal tar headspace vapors or field soil vapors were identified by comparing the retention time data from total ion chromatograms and mass spectral data of the sample peaks to known standards for the target analytes or to a mass spectral database for non-target analytes. The modified EPA Method TO-15 used by the Wadsworth Center Laboratory was for non-halogenated compounds on the standard NYS DOH Wadsworth Center Laboratory analyte list. In addition, the target analyte list included the following compounds, which are potential coal tar-associated compounds: 1) thiophene; 2) 1,2,3-trimethylbenzene; 3) 1,2,4-trimethylbenzene; 4) 1,3,5-trimethylbenzene; 5) indane; 6) indene; and 6) naphthalene. The total number of compounds on the target analyte list was 51.

The information presented in the total ion chromatograms was also reduced into various hydrocarbon family groups through the creation of *extracted ion chromatograms* (EICs). The creation of an EIC is based on the principle that specific ion fragments are indicators of certain classes of hydrocarbon compounds. Using this approach, and following method ASTM E1618, six hydrocarbon groups based on their representative fragmentation ions were reported for each sample: 1) alkanes: 43, 57, 71, 85; 2) cycloalkanes: 41, 55, 69, 83, 97, 98, 111, 112; 3) alkenes: 67, 68, 81, 82, 96, 109, 121; 4) benzene/alkylbenzenes: 78, 91, 105, 119, 120, 134, 148; 5) indane/tetralins: 104, 115, 117, 118, 131, 132, 145; and 6) naphthalene/alkylnaphthalenes: 128, 141, 142, 155.

Data Analysis

The laboratory-generated coal tar vapors were compared to the field soil vapor samples using two approaches. First, the detected target analytes were used to compare the laboratory coal tar vapor results generated at 10°C against the deep and shallow soil vapor results using histograms. This comparison is “higher-resolution” and assesses the similarity across samples on a compound-by-compound basis. The x-axis compounds for all histograms were kept constant. The x-axis compounds were sorted according to vapor pressure from left-to-right (highest vapor pressure to lowest vapor pressure). Therefore, compounds on the left-hand side are more likely to go into the vapor phase than compounds on the right-hand side. The y-axis was expressed on a log scale (\log_{10} [concentration]), as there were orders of magnitude differences among the three sample groups (laboratory-generated coal tar vapor, deep soil vapor, and shallow soil vapor). The concentration of the lowest calibration standard was 0.1 mcg/m³, which was

used as the lower limit of the y-axis on all figures. A total of six sample groups were obtained from three of the four MGP sites.

The second comparison approach assessed the six hydrocarbon groups from the EICs. This “lower-resolution” comparison evaluated whether the percentages of the six hydrocarbon groups were similar among the coal tar vapor, deep, and shallow soil vapor samples. Using a similar approach as the compound-by-compound comparisons, histograms of the percentage contributions from the six hydrocarbon groups measured in the laboratory coal tar vapor generated at 10°C were compared against the deep and shallow soil vapor samples. The x-axis hydrocarbon groups were organized in the following order (from left-to-right): alkanes, cycloalkanes, alkenes, aromatics, tetralin, and alkylnaphthalene. Therefore, samples with higher percentage contributions from non-aromatic hydrocarbons (i.e., alkanes, cycloalkanes, or alkenes) would have higher peaks in the three left-most groups, whereas samples with higher percentage contributions from aromatic hydrocarbons (i.e., aromatics, tetralin, and alkylnaphthalene) would have higher peaks in the three right-most groups. Samples with large percentage contributions of non-aromatic hydrocarbons are more closely associated with common petroleum distillates; whereas coal tar composition is largely more pyrogenic, resulting in larger percentage contributions of aromatics (Electric Power Research Institute [EPRI] 2000; NYS DOH 2003a).

Results and Discussion

Significant Compounds in MGP Coal Tar Vapor

The significant compounds in the MGP tar vapor were determined by evaluating the 51 target analytes that were used in the NYS DOH Wadsworth Center Laboratory modified EPA Method TO-15 analysis. Analytes were considered present if they were reported above the method detection limit (MDL), meaning that they were detected at any concentration. Compounds detected in only a few of the tar samples were considered “site-specific”, and therefore of limited value to the broader classification of a coal tar signature. Compounds detected in four or more of the eight laboratory-generated coal tar vapor samples at each temperature (i.e., 50% to 100% detection frequency) were considered more representative of coal tar vapor. When the 50% detection frequency criteria were applied, a total of 24 compounds were detected at 10°C and 29 compounds detected at 50°C. Overall, the compounds identified as being most frequently detected in coal tar vapor are provided in Table 1.

Comparing Coal Tar Vapor and Field Soil Vapor

Figure 1 shows the stacked histograms for one of the sample groups from one MGP site. Similar results were observed for the other five sample groups (figures not shown). In an

Table 1. Detection frequency for compounds detected in at least 50% of the laboratory-generated coal-tar vapors at 10°C and 50°C using EPA Method TO-15

Target Compounds: $\mu\text{g}/\text{m}^3$	Molecular Weight ¹ (g/mol)	Boiling Point ¹ (°C)	Vapor Pressure ¹ (Pa)	Measured at 10°C			Measured at 50°C		
				n	ND	% Detected	n	ND	% Detected
Benzene	78.1	80.0	12,600	8	2	75	8	2	75
Thiophene	84.1	84.0	10,600	8	5	38	8	4	50
Methylcyclohexane	98.2	100.9	6,130	8	5	38	8	4	50
Toluene	92.1	110.6	3,790	8	4	50	8	1	88
n-Octane	114.2	125.6	1,880	8	4	50	8	3	63
Ethylcyclohexane	112.2	131.9	1,710	8	3	38	8	4	50
Ethylbenzene	106.2	136.1	1,280	8	3	63	8	0	100
m,p-Xylene	106.2	139.1	1,110	8	3	63	8	0	100
o-Xylene	106.2	138.5	1,070	8	2	75	8	0	100
Styrene	104.2	145.0	853	8	3	63	8	0	100
Isopropylbenzene	120.2	152.4	600	8	6	25	8	4	50
n-Nonane	128.3	150.8	593	8	3	63	8	1	88
1,2,4-Trimethylbenzene	120.2	169.3	280	8	1	88	8	0	100
1,3,5-Trimethylbenzene	120.2	164.7	280	8	1	88	8	0	100
1,2,3-Trimethylbenzene	120.2	176.1	225	8	1	88	8	0	100
a-Methylstyrene	118.2	165.4	200	8	3	63	8	0	100
p-Isopropyltoluene	134.2	177.0	200	8	4	50	8	2	75
Indane	118.2	177.9	196	8	1	88	8	0	100
n-Decane	142.3	174.1	191	8	2	75	8	1	88
trans-Decahydronaphthalene	138.3	187.3	160	8	2	75	8	0	100
1,3-Diethylbenzene	134.2	181.1	151	8	2	75	8	0	100
Indene	116.2	182.0	147	8	0	100	8	0	100
1,2,4,5-Tetramethylbenzene	134.2	196.8	70	8	2	75	8	0	100
n-Undecane	156.3	195.9	55	8	1	88	8	0	100
1,2,3,4-Tetrahydronaphthalene	132.2	103.0	50	8	3	63	8	1	88
n-Dodecane	170.3	216.3	18	8	1	88	8	0	100
Naphthalene	128.2	217.9	11	8	0	100	8	0	100
2-Methylnaphthalene	142.2	241.1	7.3	8	0	100	8	0	100
n-Propylbenzene	120.2	159.0	0.3	8	6	25	8	3	63
Number detected $\geq 50\%$						24			29

Target compounds are sorted according to decreasing vapor pressure (i.e., from highest to lowest); ¹EPA (2013)

ideal soil system (i.e., homogenous, vapor-permeable soil, with no additional sources of hydrocarbons besides the coal tar source), concentrations in soil vapor should decrease as the distance from the coal tar source increases (i.e., moving upward in the soil column from deep to shallow). The laboratory coal tar vapor extraction temperature at 10°C was used for comparison to the field soil vapor measurements rather than the 50°C extraction temperature because this temperature was representative of the mesic soil temperature of New York State (United States Department of Agriculture [USDA] 2013). However, the laboratory sample likely represents the maximum number of compounds and highest concentrations that could potentially partition from the tar into the vapor phase under normal environmental conditions. The reason for this is that *in situ* coal tar would become “armored” or “crusted” on its surface due to preferential loss of lighter compounds via volatilization and solubilization from exposure in the environment for decades. In contrast, the sampling and preparation for analysis would tend to reduce this effect and render the coal tar sample more volatile than the original *in situ* source. When viewed

in this context, two interesting observations are evident following a review of Figure 1 and the other five sample groups:

1. There was often little relationship between the specific compounds identified in the laboratory coal tar vapor generated at 10°C and the field soil vapor measurements. In addition, concentrations of compounds in shallow soil vapor samples were either non-detectable or substantially lower than those found in deeper samples, suggesting attenuation in the vadose zone.
2. In general, the lower molecular weight and higher vapor pressure mono-aromatics such as benzene and toluene were the compounds that were consistently detected in the shallow soil vapor samples. The higher molecular weight and lower vapor pressure compounds that were specifically targeted in this study (e.g., 1,2,3-trimethylbenzene; 1,2,4-trimethylbenzene; 1,3,5-trimethylbenzene; indane; indene; and naphthalene) were rarely detected in the shallow soil vapor sample.

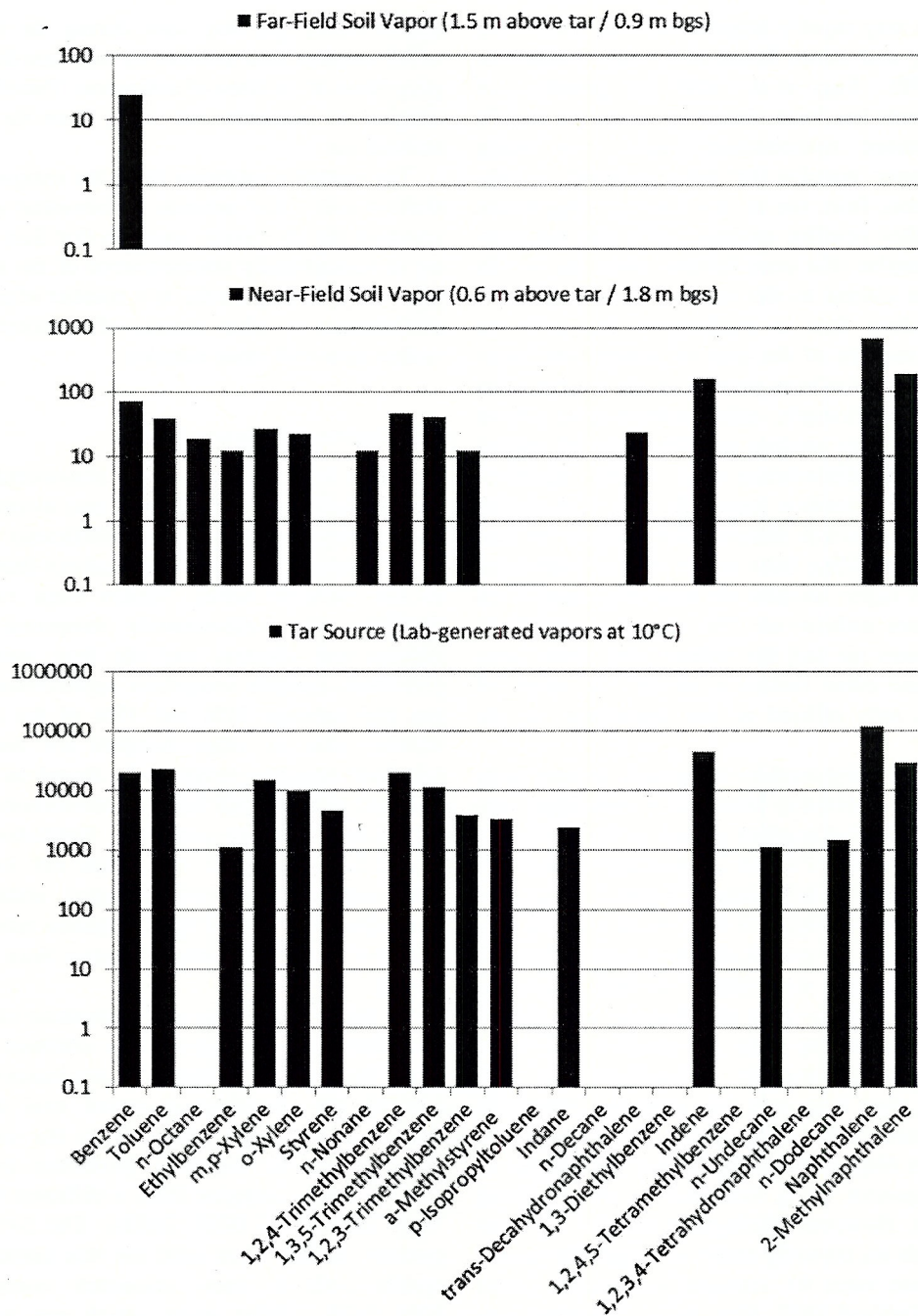


Figure 1. Graphs of comparisons for the measured EPA Method TO-15 concentrations of select analytes for: 1) laboratory-generated coal tar vapor at 10°C (bottom); 2) deep soil vapor, 0.6 m above the source/1.8 m below ground surface (middle); and 3) shallow soil vapor, 1.5 m above the source/0.9 m below ground surface (top) for one of the sample groups. Analytes are sorted from higher to lower vapor pressure.

The lack of relationship between the compounds measured in the laboratory-generated coal tar vapor and the field soil vapor samples in the six sample groups may be attributable to biodegradation occurring at rapid rates in the vadose zone soils. Nearly all of these MGP sites

stopped operating before 1950; therefore, the *in situ* coal tar sources and the surrounding soil have been exposed to the environment for more than 60 years. At other MGP sites, it has been shown that the *in situ* microorganisms quickly adapt to degrade benzene, naphthalene, and other

hydrocarbons, and may rapidly degrade soil and groundwater concentrations, and hence lower soil vapor concentrations (Madsen 1991; Yagi et al., 2010). Degradation of volatile hydrocarbons has been shown to occur so rapidly that petroleum-related hydrocarbon vapors are rarely detected in soil vapor samples that were collected at relatively short distances from the *in situ* source (Roggemans et al., 2001). Another possible explanation is that the shallow soil vapor samples (the ones furthest from the *in situ* coal tar source but closest to the surface) do not reflect a chemical composition that is exclusively the coal tar source, but some mixture of the coal tar source and background petroleum hydrocarbons present in the vadose zone and ambient air. For example, other authors have shown that levels of benzene in outdoor air often exceed regulatory screening criteria (Hawthorne et al., 2008). However, it should be noted that helium tracer gas was used during the field investigation, which ensured that ambient air was not drawn into the sampling lines at the time of collection. Therefore, the soil vapor samples do represent vapor from the vadose zone, not ambient air. The degree of equilibration between ambient air and the vadose zone from barometric pumping and other factors is beyond the scope of this study, and is only offered as one hypothesis on the observed result.

Analogous to the compound-by-compound comparisons, Figure 2 shows little relationship between the percentage contributions from the six hydrocarbon groups in the laboratory coal tar vapor generated at 10°C and the deep and shallow soil vapor samples (note the vertical y-axis of Figure 2 shows percent composition, while in Figure 1 the vertical y-axis shows log-scale concentration). In contrast, the deep and shallow soil vapor sample compositions were similar to each other. The laboratory-generated coal tar vapor distributions were largely aromatic, while the overlying deep and shallow soil vapor samples were largely non-aromatic. If biodegradation were causing this result, then it appears that aromatic compounds are preferentially biodegraded while non-aromatic compounds persist, resulting in disproportionately higher percentages of non-aromatic compounds being measured in the overlying soil vapor samples. However, biodegradation rates for non-aromatic compounds are typically orders of magnitude greater than the degradation rates for aromatic compounds (Atlas 1981; EPA 1993; DeVaul 2007; EPA 2013). Therefore, aromatic compounds would persist, while non-aromatic compounds would be biodegraded – the exact opposite of what was observed. Another possible explanation, similar to the one described above for benzene, is the presence of non-aromatic hydrocarbons in the vadose zone and ambient air that are unrelated to the coal tar source. For example, a study of outdoor air for 200 samples collected in New York State between 1997 and 2003 showed that alkanes ranging from *n*-heptane through *n*-dodecane were detected in 34% to 71% of outdoor air samples at concentrations ranging from less than one to tens of mcg/m³ (NYS DOH 2003b). Again, it should be noted that

helium tracer gas was used during the field investigation, which ensured that ambient air was not drawn into the sampling lines at the time of collection. Therefore, the soil vapor samples do represent soil vapor from the vadose zone, not ambient air.

The overall conclusion from the comparison of deep and shallow soil vapor samples to laboratory-generated coal tar vapors in the six sample groups is that field soil vapor samples are not consistently representative of the underlying coal tar source, which may be due to a number of possible attenuation mechanisms or other sources of hydrocarbons entering the vadose zone soil vapor samples.

Distribution of Chemical Groups

The EICs were summed across non-aromatic fractions (alkanes, cycloalkanes, and alkenes) and aromatic fractions (aromatics, tetralins, and alkylnaphthalenes) to generate ratios of (% non-aromatics)/(% aromatics) [hereafter referred to as the *aromatic ratio*]. Vapors from common petroleum distillates are predominantly comprised of non-aromatic alkanes and alkenes, and the total aromatic fraction of petroleum samples comprises approximately 5% of natural gas and between 21% and 27% of the liquid fuels. Conversely, coal tar vapor samples are predominantly comprised of aromatic compounds. Based on this approach, an aromatic ratio should help to discriminate between coal tar vapors and common petroleum distillates. Coal tar vapors should have aromatic ratios that are less than 1.0 (i.e., more aromatic than non-aromatic), while common petroleum distillates should have aromatic ratios that are greater than 1.0 (i.e., more non-aromatics than aromatics [EPRI, 2000]).

To assess the ability of the aromatic ratio to reliably differentiate coal tar vapors from common petroleum distillates, the range (minimum to maximum) for the aromatic ratio in the laboratory-generated coal tar vapor samples from this study was compared to the aromatic ratios that were derived for common petroleum distillates and four coal tar vapor samples from a different MGP site in New York State (NYS DOH, 2003a). The 50°C extraction temperature results were used for this assessment so that the results could be more accurately compared against the NYS DOH (2003a) study, which was conducted at 50°C. The range for the aromatic ratio in the eight laboratory-generated coal tar vapor samples was 0.12 to 1.06, while the range in the NYS DOH (2003a) MGP site study was 0.06 to 0.23. In contrast, the aromatic ratios ranged from 2.75 to 18.92 in the common petroleum distillates that were included in the analysis. While the total number of coal tar samples is relatively small, these results show that the aromatic ratio provides good discrimination between coal tar vapor at 50°C and common petroleum distillates such as domestic natural gas, gasoline, kerosene, and #2 heating oil (Figure 3).

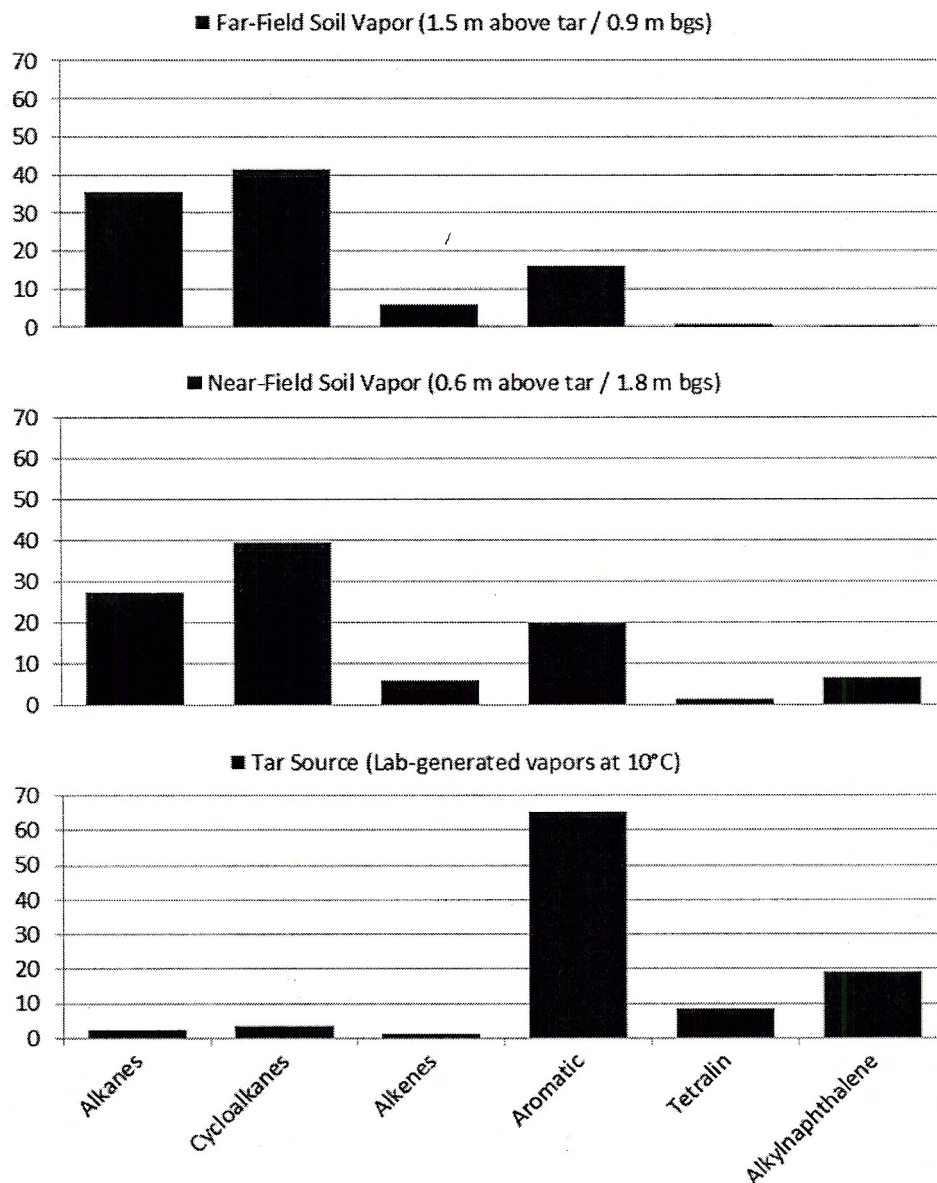


Figure 2. Graphs of comparisons for the percentages of six hydrocarbon families based on extracted ion chromatograms for: 1) laboratory-generated coal tar vapor at 10°C (bottom); 2) deep soil vapor, 0.6 m above the source/1.8 m below ground surface (middle); and 3) shallow soil vapor, 1.5 m above the source/0.9 m below ground surface (top) for one of the sample groups.

Potential Marker Compounds

Many of the 29 compounds detected in at least 50% of the laboratory-generated coal tar vapors samples generated at 50°C are also present in petroleum distillates (i.e., they are not MGP specific). For example, alkanes, cycloalkanes, alkenes, and benzene/alkylaromatics are known to be present in significant amounts (i.e., >20%) in regular gasoline, kerosene, and heating oil (NYS DOH 2003a). These compound classes encompass 20 of the 29 compounds in Table 1. Conversely, indane/tetralines and naphthalene/alkyl-naphthalenes are generally

not present in significant amounts (i.e., <5%) in these other hydrocarbon sources. Therefore, among the compounds listed in Table 1, the four compounds that could potentially be most useful as presence/absence marker compounds include: 1) indane, 2) indene, 3) naphthalene, and 4) 2-methylnaphthalene. However, these compounds were not frequently detected in the shallow soil vapor samples, which were collected less than 2.4 m above the *in situ* coal tar source. While these compounds may represent marker compounds with respect to coal tar vapor, they may be only useful as near-source indicators due to rapid attenuation in the vadose zone.

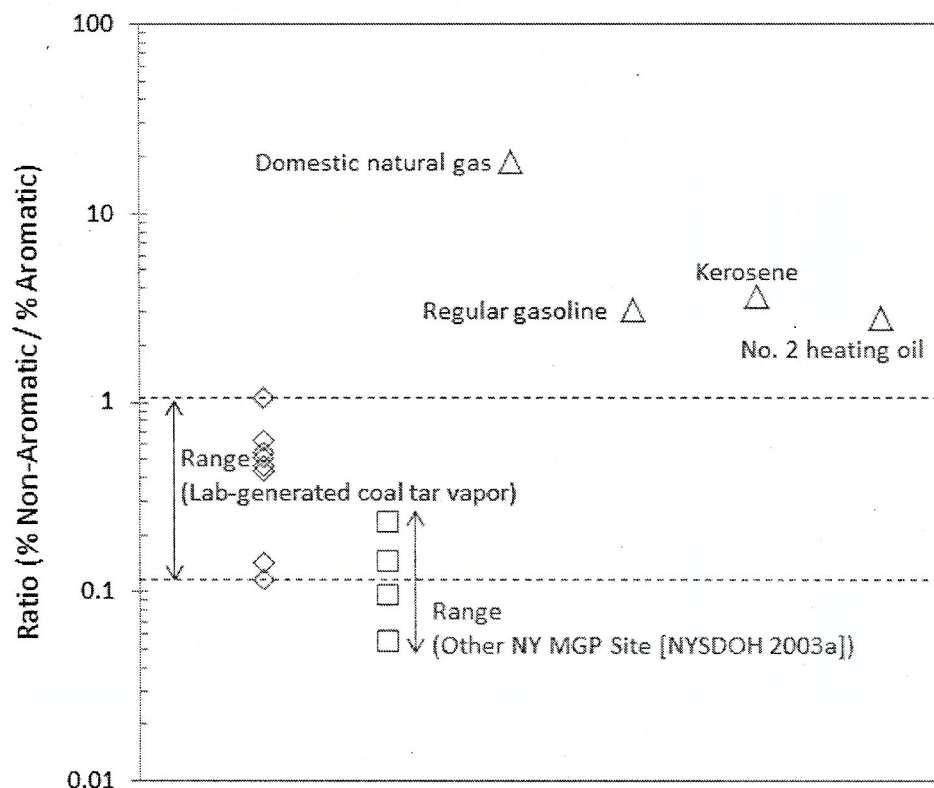


Figure 3. Graph of comparisons for showing the ratio of (% non-aromatics)/(% aromatics) for the laboratory-generated coal tar vapor samples [diamonds] (50°C), other coal tar vapor samples from New York State Department of Health (NYS DOH, 2003a) [squares] (50°C), and common petroleum distillates [triangles] (50°C). The horizontal dashed lines represent the range (minimum to maximum) of the ratios determined for the eight coal tar vapor samples analyzed as part of this study.

Conclusions

The analysis of eight field coal tar samples collected from four different MGP sites in this study showed that 24 compounds at 10°C and 29 compounds detected at 50°C were frequently detected in laboratory-generated coal tar vapors. Comparisons of the concentrations and distributions of 24 detected compounds and their respective hydrocarbon family groups between the laboratory coal tar vapors generated at 10°C and overlying deep and shallow soil vapor samples showed that there was often little relationship. Concentrations of the 24 compounds in the shallow soil vapor samples were either non-detect or substantially lower than those found in deeper samples, suggesting attenuation in the vadose zone.

This study reports the results of a limited number of sample triplet groups (i.e., laboratory coal tar offgas, deep soil vapor, and shallow soil vapor samples collected from one location), which are unlikely to fully capture the site-specific heterogeneity that may be encountered during MGP site investigations. Therefore, the results are limited in the scope of the work completed, and further study would be required to more confidently delineate source-distance relationships in the vadose zone by the collection of more samples than were collected during this study.

Funding

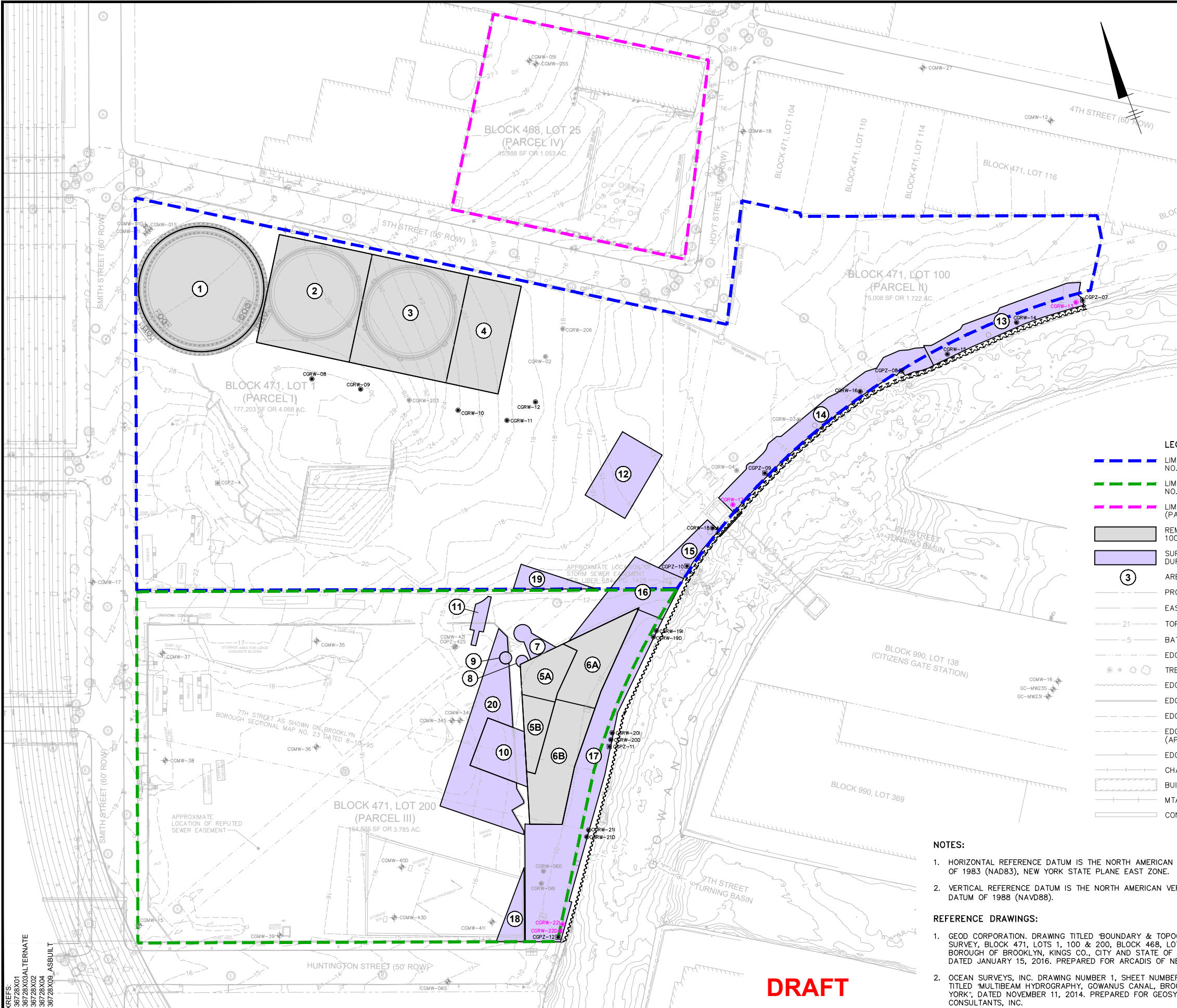
Financial support was provided by the Northeast Gas Association | NYSEARCH and National Grid. The findings and conclusions in this paper should not be construed to represent any NYS DOH agency determination or policy.

References

- Atlas, R. M. 1981. Microbial degradation of petroleum hydrocarbons: An environmental perspective. *Microbiological Reviews* 45(1): 180–209.
- DeVaul, G. E. 2007. Indoor vapor intrusion with oxygen-limited biodegradation for a subsurface gasoline source. *Environmental Science & Technology* 41(9): 3241–3248.
- Electric Power Research Institute (EPRI). 2000. *Chemical Source Attribution at Former MGP Sites*. Palo Alto, CA: EPRI, 1000728.
- Hawthorne, S. B., Azzolina, N. A., and Finn, J. T. 2008. Tracing contributions of benzene from outdoor to indoor air. *Environmental Forensics* 9:1–11.
- Hayes, T. D., Linz, D. G., Nakles, D. V., and Leuschner, A. P., eds., 1996. *Management of Manufactured Gas Plant Sites—Two-Volume Practical Reference Guide of the Gas Research Institute*. Amherst, MA: Gas Research Institute, Amherst Scientific Publishers.
- Hayes, H. C., and Benton, D. J. 2007. *The Application of Method TO-15 to Naphthalene Measurements in Indoor Air*. Paper presented at the A&WMA Symposium on Air Quality Measurement Methods and Technology (April 30–May 3, San Francisco, CA).

- Interstate Technology & Regulatory Council (ITRC). 2007. *Vapor Intrusion Pathway: A Practical Guideline, VI-1*. Washington, DC: Interstate Technology & Regulatory Council, Vapor Intrusion Team.
- Madsen, E. L., Sinclair, J. L., and Ghiorse, W. C. 1991. In situ biodegradation: Microbiological patterns in a contaminated aquifer. *Science* 252 (5007): 830–833.
- New York State Department of Environmental Conservation (NYS DEC). 2013. *MGP Program at the NYSDEC*. Available at: <http://www.dec.ny.gov/chemical/24904.html>
- New York State Department of Health (NYS DOH). 2003a, August 8. *Draft Volatilization Study of MGP Waste and Petroleum Fuels*. Albany, NY: New York State Department of Health, Center for Environmental Health and Wadsworth Center.
- New York State Department of Health (NYS DOH). 2003b. *Background Indoor/Outdoor Air Levels of Volatile Organic Compounds in homes sampled by the New York State Department of Health, 1997–2003*. Troy, NY: Bureau of Toxic Substance Assessment.
- New York State Department of Health (NYS DOH). 2006, October. *Guidance for evaluating soil vapor intrusion in the State of New York*. Albany, NY: New York State Department of Health, Center for Environmental Health, Bureau of Environmental Exposure Investigation.
- Roggemans S., Bruce C. L., Johnson P. C., and Johnson R. L. 2001, December. Vadose zone natural attenuation of hydrocarbon vapors: An empirical assessment of soil gas vertical profile data. *American Petroleum Institute Technical Bulletin* 15.
- United States Department of Agriculture (USDA). 2013, January. *Soil Temperature Regime Map*. U.S. Department of Agriculture, Natural Resources Conservation Service. Available at: http://www.nrcs.usda.gov/wps/portal/nrcs/detail/soils/use/?cid=nrcs142p2_054019
- United States Environmental Protection Agency (US EPA). 1993, May. *Behavior and Determination of Volatile Organic Compounds in Soil: A Literature Review*. Research Triangle Park, NC: Exposure Assessment Research Division, US EPA, 600-R-93-140.
- United States Environmental Protection Agency (US EPA). 1999a, May. *A Resource for MGP Site Characterization and Remediation*. Washington, DC: Office of Solid Waste and Emergency Response, US EPA, (5102G) 542-R-99-005.
- United States Environmental Protection Agency (US EPA). 1999b, January. *Compendium Method TO-15: Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry (GC/MS)*. Washington, DC: Center for Environmental Research Information Office of Research and Development, US EPA, 625/R-96/010b.
- United States Environmental Protection Agency (US EPA). 2013. *Estimation Programs Interface Suite for Microsoft Windows, version 4.11*. United States Environmental Protection Agency, Washington, DC: US EPA
- Yagi, J. M., Neuhauser, E. F., Ripp, J. A., Mauro, D. M., and Madsen, E. L. 2010. Subsurface ecosystem resilience: Long-term attenuation of subsurface contaminants supports a dynamic microbial community. *ISME Journal*, 4:131–143.

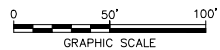
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EXCAVATION SCHEDULE				
EXCAVATION AREA	APPROX. EXCAVATION ELEVATION (FEET NAVD88)	APPROX. EXCAVATION DEPTH (FEET BGS)	ESTIMATED EXCAVATION VOLUME (CY)	EXCAVATION PURPOSE
1	15.0	14.0	6,445	SOURCE AREA/STRUCTURE REMOVAL
2	3.0	26.0	9,975	SOURCE AREA/STRUCTURE REMOVAL
3	2.0	26.0	11,725	SOURCE AREA/STRUCTURE REMOVAL
4	2.0	22.5	4,450	SOURCE AREA/STRUCTURE REMOVAL
5A	-10.0	20.5	1,565	SOURCE AREA/STRUCTURE REMOVAL
5B	-10.0	20.5	1,270	SOURCE AREA/STRUCTURE REMOVAL
6A	-10.0	20.5	2,810	SOURCE AREA/STRUCTURE REMOVAL
6B	-10.0	20.5	3,975	SOURCE AREA/STRUCTURE REMOVAL
7	8.5	4.0	100	SOURCE AREA/STRUCTURE REMOVAL
8	7.0	4.0	15	SOURCE AREA/STRUCTURE REMOVAL
9	8.0	4.0	20	SOURCE AREA/STRUCTURE REMOVAL
10	2.0	10.0	950	SOURCE AREA/STRUCTURE REMOVAL
11	-2.0	16.5	310	SOURCE AREA/STRUCTURE REMOVAL
12	-8.0	22.0	2,770	SOURCE AREA/STRUCTURE REMOVAL
13	3.0	5.0	695	BULKHEAD BARRIER WALL INSTALLATION
14	-2.0	13.0	2,415	BULKHEAD BARRIER WALL INSTALLATION
15	-2.0	13.0	610	BULKHEAD BARRIER WALL INSTALLATION
16	4.0	9.0	1,230	BULKHEAD BARRIER WALL INSTALLATION
17	4.0	6.0	2,645	BULKHEAD BARRIER WALL INSTALLATION
18	4.0	11.0	430	BULKHEAD BARRIER WALL INSTALLATION
19	10.0	5.0	195	TEMPORARY FABRIC STRUCTURE INSTALLATION
20	10.0	5.0	1,235	TEMPORARY FABRIC STRUCTURE INSTALLATION

LEGEND:

- LIMIT OF BROWNFIELD CLEANUP PROGRAM SITE NO. C224012 (PARCELS I AND II)
- LIMIT OF BROWNFIELD CLEANUP PROGRAM SITE NO. C224012B (PARCEL III)
- LIMIT OF STATE SUPERFUND SITE NO. 224012 (PARCEL IV)
- REMEDIAL EXCAVATION AREA INCLUDED IN 100% REMEDIAL DESIGN REPORT (APPROXIMATE)
- SUPPLEMENTAL EXCAVATION AREA COMPLETED DURING REMEDIATION PROJECT (APPROXIMATE)
- 3 AREA IDENTIFIER
- PROPERTY LINE (APPROXIMATE)
- EASEMENT LINE (APPROXIMATE)
- 21--- TOPOGRAPHIC CONTOUR (1-FOOT INTERVAL)
- 5--- BATHYMETRIC CONTOUR (1-FOOT INTERVAL)
- EDGE OF WATER
- * TREE
- EDGE OF VEGETATION
- EDGE OF PAVEMENT/CONCRETE
- EDGE OF GRAVEL
- EDGE OF SOIL/AGGREGATE PILE (APPROXIMATE)
- EDGE OF BULKHEAD
- CHAIN-LINK FENCE
- BUILDING
- MTA RAILROAD TRACK
- CONCRETE WALL
- BOLLARD
- SIGN
- UTILITY POLE
- HYDRANT
- SANITARY SEWER MANHOLE
- STORM SEWER MANHOLE
- WATER MANHOLE
- GAS MANHOLE
- TELECOMMUNICATIONS MANHOLE
- ELECTRICAL MANHOLE
- MANHOLE (TYPE UNKNOWN)
- CATCH BASIN
- ELECTRICAL BOX
- WATER VALVE
- GAS VALVE
- NEW PIEZOMETER INCLUDED IN 100% REMEDIAL DESIGN REPORT
- EXISTING PIEZOMETER
- EXISTING MONITORING WELL
- NEW RECOVERY WELL INCLUDED IN 100% REMEDIAL DESIGN REPORT
- ADDITIONAL NEW RECOVERY WELL INSTALLED DURING REMEDIATION PROJECT
- EXISTING RECOVERY WELL
- NEW BULKHEAD BARRIER WALL



NOTES:

- HORIZONTAL REFERENCE DATUM IS THE NORTH AMERICAN DATUM OF 1983 (NAD83), NEW YORK STATE PLANE EAST ZONE.
- VERTICAL REFERENCE DATUM IS THE NORTH AMERICAN VERTICAL DATUM OF 1988 (NAVD88).

REFERENCE DRAWINGS:

- GEOD CORPORATION. DRAWING TITLED 'BOUNDARY & TOPOGRAPHIC SURVEY, BLOCK 471, LOTS 1, 100 & 200, BLOCK 468, LOT 25, BOROUGH OF BROOKLYN, KINGS CO., CITY AND STATE OF NEW YORK', DATED JANUARY 15, 2016. PREPARED FOR ARCADIS OF NEW YORK, INC.
- OCEAN SURVEYS, INC. DRAWING NUMBER 1, SHEET NUMBER 2 OF 3, TITLED 'MULTIBEAM HYDROGRAPHY, GOWANUS CANAL, BROOKLYN, NEW YORK', DATED NOVEMBER 11, 2014. PREPARED FOR GEOSYNTEC CONSULTANTS, INC.

DRAFT

NATIONAL GRID
FORMER CITIZENS GAS WORKS MANUFACTURED GAS PLANT SITE
BOROUGH OF BROOKLYN, KINGS COUNTY, NEW YORK

SITE REMEDIATION PLAN



FIGURE
1